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Role of bond coordination and molecular volume on the dielectric constant of mixed-oxide compounds

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First-principles calculations have been employed to study clusters of Zr embedded in SiO_2. Stable complexes are found with four, six, and seven oxygens coordinated to the Zr atom. Consistent with experiment, the higher coordinated complexes are the most stable. These also have a higher density, and hence, smaller molar volume. This smaller molar volume provides an explanation of the increased dielectric constant of $Zr_xSi_{1-x}O_2$ mixed-oxide systems for small amounts of Zr ($x < 0.3$). An unusual sevenfold coordinated structure is described. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1409590]

The technology driven search[1] for a replacement of SiO_2 in applications such as transistor gate insulators and memory cell and coupling capacitor dielectrics has lead to a study of a wide range of materials. For a given material to be chosen it should, ideally, have a large permittivity with respect to SiO_2 (say, $\varepsilon \sim 20-30$), have a large band gap (to avoid electron or hole injection from the gate electrode or substrate), and be thermally compatible with Si (i.e., remain amorphous and avoid a reaction resulting in the creation of silicides or roughened Si/insulator interfaces). At the present time no clear candidate has emerged but interesting results have been obtained with $Zr_xSi_{1-x}O_2$ ($x < 0.3$) mixed oxides,[2–4] where the dielectric constant is ~ 11 for $x \sim 0.2$. The dielectric constant increase is probably too small with respect to SiO_2 to merit the industrial investment necessary to change technology to this material. However, we note that on a simple linear extrapolation basis one would expect the dielectric constant of this compound to be ~ 7 so that some clear and important enhancement is occurring. Note that enhanced dielectric constants are also observed in other mixed-oxide compounds[5] such as Ta_2O_5/TiO_2 so that this effect is not limited to the ZrO_2/SiO_2 system. What is the physical origin of this enhancement and can one engineer it in more technologically useful materials?

The dielectric constant of a mixed-oxide system can be treated in the framework of the oxide additivity rule[6,7] where the dielectric constant can be expressed as

$$\varepsilon = \{1 + [8\pi/(3V_m)]\alpha_m(M_{Ax}M'_{Bp}O_{Ay+Bq})\}/\{1$$
$$- [4\pi/(3V_m)]\alpha_m(M_{Ax}M'_{BP}O_{Ay+Bq})\}, \quad (1)$$

where $\alpha_m(M_{Ax}M'_{Bp}O_{Ay+Bq})$ is the molar polarizability for the mixed-oxide M_xO_y/M'_pO_q (written as a weighted sum of the individual molar polarizabilities[6,7]) and V_m is the molar volume of the mixed-oxide molecule. Since the denominator of Eq. (1) contains a negative sign, the size of the product of the molar polarizability and of the molar volume with respect

to unity are clearly crucial in determining the magnitude of the mixed-oxide dielectric constant. In the following, we report the results of a theoretical investigation of the behavior of the molar volume in mixed-oxide compounds with specific reference to the ZrO_2/SiO_2 system. We demonstrate that bonding coordination plays a crucial role and that in fact high coordination leads to substantial molar volume decreases, which should result in enhanced dielectric constants. The importance of volume effects, as explicited in Eq. (1), was neglected in an earlier explanation of the origin of the enhanced dielectric constant.[4] Furthermore, in the model outlined in Ref. 4, fourfold coordination was extensively evoked whereas, as we shall demonstrate, our conclusions are to the contrary that higher coordination is important in ZrO_2/SiO_2 binary-oxide compounds. The importance of all these factors will become evident in the following.

We have used first-principles theory to study clusters simulating a Zr atom embedded in SiO_2. Two types of calculations were performed—density functional theory (DFT) based on the B3LYP functional using the North West Chemistry program[8] and second-order many-body perturbation theory based on a Hartree–Fock reference (MP2) using the Gaussian atomic and molecular electronic structure system program.[9] To allow the study of fairly large clusters, the effective core potentials[10] were employed in all calculations along with the corresponding valence shell basis set.[10]

Initial clusters considered a central Zr coordinated to oxygen neighbors that were bonded to Si next neighbors. The three remaining Si bonds on each Si were terminated with hydrogen atoms. Complexes with different numbers of oxygens coordinated to the Zr were found, corresponding to several different local bonding schemes. Stable clusters have been identified with the Zr coordinated to four, six, and seven oxygens. The simplest clusters are the four- and six-coordinated systems with formulas $Zr(OSiH_3)_4$ and $Zr(OSiH_3)_4[O(SiH_3)_2]_2$. In the four-coordinated cluster the Zr occupies a simple substitutional tetrahedral Si site. Three different six-coordinated structures have been found which vary only in the relative orientation of the $H_3SiOSiH_3$

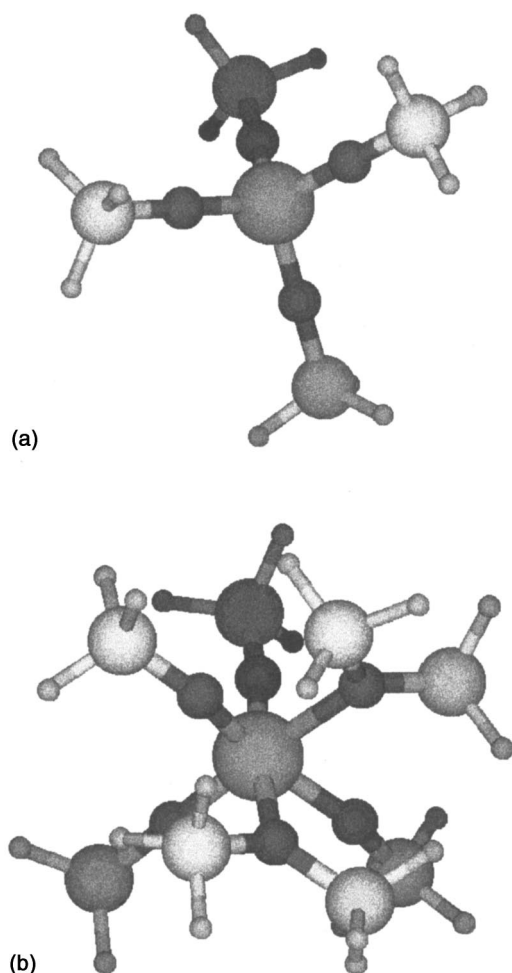[a]Electronic mail: devine@chtm.unm.edu

(a)

(b)

FIG. 1. Optimized structures with Zr coordinated to four and six oxygens. The central atom is zirconium, the small atoms are oxygens, and the remaining, large atoms are silicons.

FIG. 2. Stable seven-coordinated Zr structure.

groups. Figure 1(a) shows the most stable complex for four nearest-neighbor oxygens and Fig. 1(b) for six oxygens. Both DFT and MP2 calculations indicate that the six-coordinated structure is more stable than the four-coordinated structure plus two uncoordinated $H_3SiOSiH_3$ units. Energetically, the difference is about 0.5 eV in the DFT case and 1.5 eV in the MP2 case.

From examination of these two types of local environments it is apparent that Zr's ability to coordinate to more than four oxygens causes a significant change in the local network [Figs. 1(a) and 1(b)]. The four-coordinated system has four first-nearest-neighbor Si atoms and the following layer would involve 12 oxygen atoms. The six-coordinated system has eight first-nearest-neighbor Si atoms and a resulting 24 oxygens in the next-nearest-neighbor layer—twice the number from the four-coordinated system. This higher local network density would give rise to a smaller molar volume for these Zr sites and, as a consequence, give larger ε [Eq. (1)]. Based on the above models, the density computed inside a sphere with radius 5.0 Å centered on the Zr atom is 1.6 times larger for the six-coordinated structure than for the four-coordinated structure. This increase in density for high coordination of the Zr clearly corresponds to a decrease in molar volume V_m, and therefore, with reference to Eq. (1), an increase in the dielectric constant of the material.
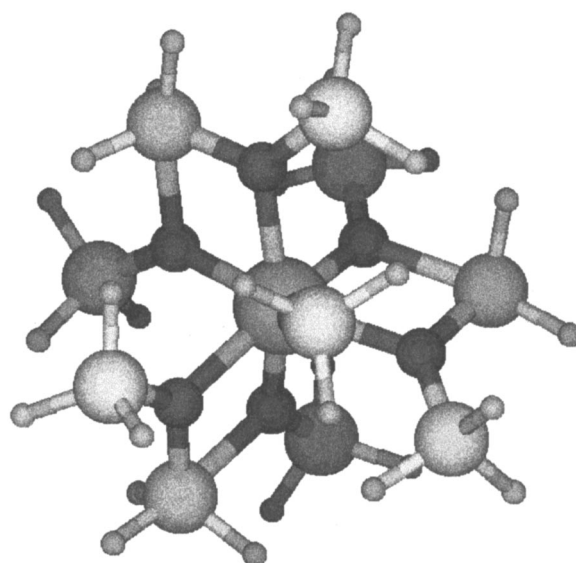
A very interesting seven-coordinated structure has also been found. Starting the calculation from a structure similar to the six-coordinated one with a formula $Zr(OSiH_3)_4[O(SiH_3)_2]_3$ resulted in a rearrangement of the ligands to produce the structure shown in Fig. 2. In this optimized structure three of the $OSiH_3$ ligands have combined with the three $H_3SiOSiH_3$ ligands to form three unusual bidentate ligands (two connections to the Zr). Each of these new structures contains a five-coordinate Si atom, suggesting the presence of a negative charge and significant charge separation from the Zr to the Si atoms. This structure is stable in both DFT and MP2 calculations but not in the Hartree–Fock method. When the total energy is compared to the six-coordinate structure plus an unattached $H_3SiOSiH_3$, the DFT approach indicated the six-coordinate structure is more stable but the MP2 calculations favor the seven-coordinate structure. The effects of embedding this cluster into a larger network will need to be included to accurately determine its relative stability and further calculations are ongoing.

The further increased coordination of the Zr again causes the local density to be increased (now 30 second-neighboring oxygens), which will enhance the dielectric constant through a decrease in V_m. The density inside the 5.0 Å sphere is now 1.9 times the four-coordinated density. In addition, the aforementioned charge delocalization should have the effect of increasing the polarizability term, α_m, in Eq. (1)—also increasing the dielectric constant for this type of system.

It is worthwhile at this point to compare the conclusions that can be drawn from the calculations with those extracted from experiments. From extended x-ray absorption fine structure measurements on xerogels[11] it has been ascertained that the O coordination around the Zr atoms is $\geqslant 7$ and this for concentrations of $Zr_{0.1}Si_{0.9}O_2$. For trace quantities (~2000 ppm) of Zr in a variety of predominantly SiO_2-based glasses, the first-nearest-neighbor O coordination has been found[12] to be 6. Finally, over a range of concentrations of $Zr_xSi_{1-x}O_2$ compounds, the O coordination has again been found[13] to be 6. It is, therefore, tempting to believe that the

zirconium first-nearest-neighbor O coordination in the mixed ZrO_2/SiO_2 oxides is 6.

The calculations presented enable us to conclude that the effective molar volume is directly, and rather critically, related to coordination of the Zr atom in the SiO_2 network. Therefore, one can anticipate that, in general, dissolving high-coordination atoms into low-coordination networks such as SiO_2 will inevitably lead to an anomalously rapid decrease in the molar volume/increase in the molar density around the dissolved atom. This molar volume decrease will manifest itself in the dielectric constant of the network. At the present time we are unable to absolutely quantify the density changes expected in the "real" ZrO_2/SiO_2 mixture. Further calculations on the ZrO_2/SiO_2 network are underway on even larger clusters to (1) study the stability and energetics of forming connections in the a-SiO_2 materials and (2) to add additional Zr atoms, i.e., extend the size of the clusters to include more than one Zr atom.

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